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Irreversible port-Hamiltonian systems: a general formulation of irreversible processes with application to the CSTR

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Abstract

In this paper we suggest a class of quasi-port Hamiltonian systems called Irreversible port Hamiltonian Systems, that expresses simultaneously the first and second principle of thermodynamics as a structural property. These quasi-port Hamiltonian systems are defined with respect to a structure matrix and a modulating function which depends on the thermodynamic relation between state and co-state variables of the system. This modulating function itself is the product of some positive function γ and the Poisson bracket of the entropy and the energy function. This construction guarantees that the Hamiltonian function is a conserved quantity and simultaneously that the entropy function satisfies a balance equation containing an irreversible entropy creation term. In the second part of the paper, we suggest a lift of the Irreversible Port Hamiltonian Systems to control contact systems defined on the Thermodynamic Phase Space which is canonically endowed with a contact

structure associated with Gibbs' relation. For this class of systems we have suggested a lift which avoids any singularity of the contact Hamiltonian function and defines a control contact system on the complete Thermodynamic Phase Space, in contrast to the previously suggested lifts of such systems. Finally we derive the formulation of the balance equations of a CSTR model as an Irreversible Port Hamiltonian System and give two alternative lifts of the CSTR model to a control contact system defined on the complete Thermodynamic Phase Space.
Keywords: Irreversible thermodynamics, Entropy, Port-Hamiltonian system, Contact structure, System theory, Chemical reactor

1. Introduction

The use of physical invariants such as the total energy, momentum or mass, has lead to a huge variety of efficient methods for the modelling, simulation and control of physical systems. These invariants structure the dynamical models of physical systems. For mechanical systems, arising from variational formulations, Lagrangian and *Hamiltonian systems* are derived (Arnold, 1989) and have been extended to control systems representing open physical systems called controlled Hamiltonian or Lagrangian systems or input-output Hamiltonian systems (Brockett, 1977; van der Schaft, 1986), (Marsden, 1992, chap. 7). For the Hamiltonian systems, the Hamiltonian function is a dynamical invariant (other invariants may arise from its symmetries) and is often equal to the (free) energy of the mechanical system. The other fundamental invariant of these systems is its geometric structure, the *symplectic structure* which is defined by a canonical skew-symmetric ten-

sor on the co-state variables of the system and defined in practice, by some skew-symmetric matrix, called *structure matrix*. For physical systems, it represents the canonical reversible coupling between two physical domains (e.g. the elastic and the kinetic energy exchange in a perfect oscillator).

These Hamiltonian formulations may be extended to electrical systems and networks by considering Hamiltonian systems defined with respect to a generalization of symplectic structure, i.e. *Poisson structures* (Arnold, 1989) which may be associated with the topology of the system such as graphs of electrical circuits or the kinematic relations of a mechanism for instance (Maschke et al., 1995; van der Schaft and Maschke, 2009) and whose extension to open or controlled physical systems is called *port Hamiltonian Systems* (Maschke and van der Schaft, 1992; van der Schaft and Maschke, 1995; Duindam et al., 2009).

However when irreversible phenomena have to be described then this Hamiltonian frame is not adapted anymore. The Hamiltonian systems have to be completed with an additional term representing the dissipation leading to a system composed of the sum of a Hamiltonian and a gradient system (van der Schaft, 2004) which is defined by a Riemannian metric which is defined in practice by some symmetric positive matrix. For electro-mechanical systems which are assumed to be in isothermal conditions and for which it is not necessary to represent the thermal domain, these systems are *dissipative Hamiltonian systems* with a well defined geometric structure generalizing the Poisson structure (Ortega and Planas-Bielsa, 2004).

When, as it is the case in chemical engineering, furthermore the energy (or equivalently the entropy) balance equation have to be included in the

model, then the preceding models cannot be used anymore. And a variety of models have been suggested; their main characteristics is to represent all balance equations of the models, including the total energy and entropy balance equations. Two main classes of systems have been suggested, *quasi-gradient systems* (Favache and Dochain, 2010; Favache et al., 2011) and *quasi-Hamiltonian systems* (Grmela and Öttinger, 1997; Öttinger and Grmela, 1997; Mushik et al., 2000; Hoang et al., 2011, 2012; Ramirez et al., 2009; J. K. Johnsen and Allgöwer, 2008), the latter being the subject of this paper.

In the first part of the paper, we shall elaborate on the definition of these quasi-Hamiltonian systems. Indeed in order to represent simultaneously the total energy and entropy balance, a simple example of heat transfer phenomena will be used to show that these formulations are not dissipative Hamiltonian as the matrices defining the symmetric and skew-symmetric tensors are functions of the co-state variables which destroys the linearity associated with tensors (Eberard et al., 2007)[1]. But we shall characterize this nonlinearity of the structure matrices in a more precise way, as a function depending on the co-state variables. We suggest a quasi-Hamiltonian system called *Irreversible Port Hamiltonian System* (IPHS) defined with respect to a skew-symmetric structure matrix composed of the product of a constant skew-symmetric matrix with this modulating function and give a physical interpretation.

In the second part of the paper, we use an alternative formulation based

[1]Note that this is also the case with the the quasi-gradient formulations in Favache and Dochain (2010); Favache et al. (2011).

on an intrinsic geometric structure associated with Gibbs' relations, characterized as the set of tangent planes and defined as *contact structure* (Hermann, 1973, 1974; Arnold, 1989). This geometric structure is intrinsic to the Thermodynamic Phase Space (TPS) composed of all extensive and intensive variables of a thermodynamic system in the same way as the symplectic structure is intrinsic to the configuration-momentum space of a mechanical system and is actually closely related to it. Following earlier work on the formulation of reversible (Mrugała, 1993) and irreversible transformations (Grmela and Öttinger, 1997; Grmela, 2001) for closed and its extensions to open thermodynamic systems (Eberard et al., 2005, 2007; Favache et al., 2010, 2009), we shall express the Irreversible Port Hamiltonian Systems as *control contact systems* on the complete Thermodynamic Phase Space.

In the third part, we consider a Continuous Stirred Tank Reactor (CSTR) model and firstly remind different dissipative Hamiltonian formulations of the balance equations, showing precisely the dependence of the structure matrices on the co-state variables. Secondly we derive the formulation of the CSTR as an Irreversible Port Hamiltonian System and give physical interpretation of the Poisson structure matrix in terms of the stoichiometry of the reaction and the modulating function and in its relation with the irreversible entropy creation. Finally the lift of this system to the complete Thermodynamic Phase Space is performed and an alternative is discussed.

2. Port-Hamiltonian formulation of open thermodynamic systems

2.1. Reminder on port-Hamiltonian systems

Port Hamiltonian systems (PHS) (Maschke and van der Schaft, 1992) have been widely used in modelling and passivity-based control (PBC) of mechanical and electro-mechanical system (Duindam et al., 2009; Ortega et al., 2008). On the state space $\mathbb{R}^n \ni x$, a PHS is defined by the following state equation,

$$\dot{x} = J(x)\frac{\partial U}{\partial x}(x) + g(x)u(t) \tag{1}$$

where $U : \mathbb{R}^n \to \mathbb{R}$ is the Hamiltonian function, $J(x) \in \mathbb{R}^n \times \mathbb{R}^n$ is a state-dependent skew-symmetric matrix, $g(x) \in \mathbb{R}^m \times \mathbb{R}^n$ is the input matrix and $u(t) \in \mathbb{R}^m$ is a time dependent input. If it satisfies some integrability conditions, the Jacobi identities (Libermann and Marle, 1987), the skew-symmetric matrix $J(x)$ is the definition in coordinates of a *Poisson bracket*, that is a a map from the pairs of $C^\infty(\mathbb{R}^n)$ functions Z and G to a $C^\infty(\mathbb{R}^n)$ function denoted by $\{Z, G\}_J$ and defined as:

$$\{Z, G\}_J = \frac{\partial Z}{\partial x}^\top (x) J(x) \frac{\partial G}{\partial x}(x). \tag{2}$$

From (2), it is seen that the structure matrix $J(x)$ also defines a 2-contravariant tensor on the co-states. As a consequence, the variation of any function Z along the PHS dynamics (1) may be expressed in term of the Poisson bracket:

$$\dot{Z} = \{Z, U\}_J + \sum_{i=1}^{m} L_{g_i} Z(x)\, u_i(t),$$

where $L_{g_i} Z$ denotes the Lie derivative of Z with respect to the vector fields defined by the columns $g_i(x)$ of the input matrix $g(x)$ and is expressed in

coordinates as $L_{g_i} Z(x) = \left(\frac{\partial Z}{\partial x}\right)^T g_i(x)$. By the skew-symmetry of the matrix $J(x)$ (and its Poisson bracket), the Hamiltonian function obeys the following balance equation:

$$\dot{U} = \sum_{i=1}^{m} L_{g_i} U(x)\, u_i(t)$$

which implies that it is conserved when the input is identically 0 and also leads to the definition of outputs conjugated to the inputs: $y_i = L_{g_i} Z(x)$. For (isothermal) electro-mechanical systems, the Hamiltonian function is often chosen to be the total (free) energy.

The port-Hamiltonian system (1) is an extension of Hamiltonian systems with an input term defined by input vector fields g_i which are not necessarily Hamiltonian (Maschke and van der Schaft, 1992; van der Schaft and Maschke, 1995) and hence also an extension of control Hamiltonian systems (Brockett, 1977; van der Schaft, 1989). Notice that when the structure matrix is constant then the Jacobi identities are satisfied. This case encompasses the structure of standard Hamiltonian systems with external forces where $J = \left[\begin{smallmatrix} 0_m & I_m \\ -I_m & 0_m \end{smallmatrix}\right]$ (0_m denoting the square null matrix and I_m the identity matrix of dimension m). In general the structure matrices $J(x)$ and $g(x)$ are defined by the *topology* of the system, that is the interconnection relations in the system such as Kirchhoff's laws of circuits (Maschke et al., 1995), the kinematic and static relations of a mechanical system (Maschke and van der Schaft, 1997), mass flow circuits and chemical reaction kinetics in mass balance systems (Ortega et al., 2000; Sbarbaro and Ortega, 2007; Bao and Lee, 2007; Dörfler et al., 2009), stoichiometric coefficents in chemical reaction networks (Oster and Perelson, 1974; Otero-Muras et al., 2008) or general interconnection relations on complexes (van der Schaft and Maschke, 2009).

The properties of Poisson brackets such as its skew-symmetry or existence of an integrable kernel correspond to the existence of conservation laws or balance equations for open systems and are the base of the derivation of passivity-based control laws using these invariants (Ortega et al., 2002, 2008; Duindam et al., 2009).

2.2. Formulation of the second principle

For thermodynamically consistent models of physical systems expressing some irreversible phenomena, i.e., transformations that involves irreversible entropy creation and the explicit formulation of the associated energy or entropy balance equation, it is not sufficient to express the conservation of energy but it is also necessary to express the irreversible entropy creation associated with the irreversible transformation as a *system theoretic property*.

Consider the Hamiltonian system defining the *drift vector field of the port Hamiltonian system* (1). We have seen that, by skew-symmetry of the Poisson bracket, the total energy of the drift system satisfies the conservation law $\frac{dU}{dt} = \{U, U\}_J = 0$. Now, in order to express the second principle, there should be a second entropy-like $C^\infty(\mathbb{R}^n)$ function S, which expresses the irreversible entropy creation by the balance equation

$$\frac{dS}{dt} = \{S, U\}_J = \frac{\partial S}{\partial x}^\top J(x) \frac{\partial U}{\partial x} = \sigma(x) \geq 0$$

with a strict inequality when $\frac{\partial U}{\partial x} \neq 0$. That implies that the structure matrix J should depend on the gradients of both the Hamiltonian and the entropy functions. For a simple thermodynamic system however, the internal energy may be chosen as the Hamiltonian function and the entropy may be chosen as a coordinate. As a consequence the structure matrix is expressed as a

function of the gradient of the Hamiltonian function $J\left(x, \frac{\partial U}{\partial x}\right)$ (Eberard et al., 2007). However if the skew-symmetry of the structure matrix J is an explicit function of the gradient $\frac{\partial U}{\partial x}$, the drift dynamic $J\left(x, \frac{\partial U}{\partial x}\right)\frac{\partial U}{\partial x}$, is a *nonlinear function* in the gradient $\frac{\partial U}{\partial x}(x)$. In this sense the symplectic structure of the PHS, given by the Poisson tensor associated with the structure matrix $J(x)$, is destroyed. This is the reason why for models of physical systems expressing simultaneously the energy conservation and the irreversible entropy creation, as it occurs in chemical engineering for instance, the Hamiltonian formulation has been questioned.

It is interesting to note that in other formulations when the Hamiltonian is chosen to be the total entropy of the system (Favache et al., 2010), or the availability function (Hoang et al., 2011) or in the GENERIC formulation (Jongschaap and Öttinger, 2004), the structure matrices also depend explicitly on the gradient of the generating functions.

2.3. Irreversible PHS

In this section we shall define an extension of port Hamiltonian systems defined with respect to a skew-symmetric structure matrix which on the one hand side represents the topology of the system but on the other hand side allows to express both the first and second principles of thermodynamics. The means to achieve the latter property is to derive the structure matrix as a function of the gradients of two functions, being for physical systems the energy and the entropy functions.

2.3.1. Definition

We define hereafter a quasi-Hamiltonian system, called Irreversible Port Hamiltonian system, generated by some Hamiltonian function U, with respect to a skew-symmetric structure matrix depending on its gradient as well as on the gradient of some additional function, a generalized entropy function denoted by S, as follows.

Definition 1. *An* Irreversible Port Hamiltonian System *(IPHS) is defined by the dynamic equation*

$$\dot{x} = R\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}\right) J \frac{\partial U}{\partial x}(x) + W\left(x, \tfrac{\partial U}{\partial x}\right) + g\left(x, \tfrac{\partial U}{\partial x}\right) u \tag{3}$$

where

1. *the state variable is* $x(t) \in \mathbb{R}^n$*, the input variable is* $u(t) \in \mathbb{R}^m$*,*
2. *the Hamiltonian function* $U \in \mathcal{C}^\infty(\mathbb{R}^n)$ *and the entropy function* $S \in \mathcal{C}^\infty(\mathbb{R}^n)$*,*
3. *The structure matrix* $J \in \mathbb{R}^n \times \mathbb{R}^n$ *is a constant skew-symmetric matrix, structure matrix of the Poisson bracket* $\{\ ,\ \}_J$*,*
4. $R = R\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}\right)$ *is the product of a positive definite function* γ *and the Poisson bracket of* S *and* U*:*

$$R\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}\right) = \gamma\left(x, \tfrac{\partial U}{\partial x}\right) \{S, U\}_J \tag{4}$$

   with $\gamma\left(x, \tfrac{\partial U}{\partial x}\right) \in \mathcal{C}^\infty(\mathbb{R}^n \times \mathbb{R}^n) \to \mathbb{R}$*, a non-linear positive function of the states and co-states of the system,*
5. *the vector field* $W\left(x, \tfrac{\partial U}{\partial x}\right)$ *and the input matrix* $g\left(x, \tfrac{\partial U}{\partial x}\right)$ *are smooth functions and define the input map, affine in the control* u*.*

2.3.2. Discussion

Let us comment the Definition 1 of irreversible port-Hamiltonian systems in the context of the dynamic models of physical systems, especially systems of mass and energy or entropy balance equations appearing for instance in models of CSTR.

Let us discuss firstly its *drift dynamics* defined by the vector field:

$$f\left(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x}\right) = R\left(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x}\right) J \frac{\partial U}{\partial x}(x) \tag{5}$$

corresponding to the model of the closed physical system. Notice that the system is an extension of Hamiltonian systems in the sense discussed in the Section 2.2. Indeed its structure matrix is:

$$\mathcal{J} = R\left(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x}\right) J \tag{6}$$

which is the product of the skew-symmetric real matrix with a function depending on the gradients of both functions U and S. From the skew-symmetry of $\mathcal{J}$, it follows that the Hamiltonian function U is a conserved quantity of the drift dynamics. Furthermore its gradient is also the generating force of this dynamics.

An obvious candidate for the Hamiltonian function U is of course the total energy of the system which is a conserved quantity. Let us notice that, in this frame it is excluded to choose as Hamiltonian $U(x)$ other thermodynamic potentials which are not conserved, like the entropy (Favache et al., 2010; Hoang et al., 2011; Grmela and Öttinger, 1997) or the availability function for closed-loop reference systems (Hoang et al., 2011). In all these latter formulations the structure matrix looses its skew-symmetry and is defined as the sum of a skew-symmetric and a symmetric matrix. We refer to the

Section 4 for a detailed discussion of the implication of the different choices in the case of models of CSTR.

Let us discuss now more in details the skew-symmetric structure matrix $\mathcal{J}$ defined in (6) as the product of a constant skew-symmetric matrix J with the function R depending on the gradients of the two functions U and S. As the skew-symmetric structure matrix J is constant, it satisfies the Jacobi identities and the vector field $J\frac{\partial U}{\partial x}$ is a Hamiltonian vector field while the autonomous dynamics $R\left(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x}\right) J\frac{\partial U}{\partial x}$ defines a quasi-Hamiltonian vector field in the sense of Section 2.2. The choice of J as a constant skew-symmetric matrix might appear as a restrictive choice which, however, might be justified by aim of representing with this matrix not only the symplectic Poisson brackets in canonical coordinates, as they arise in standard Hamiltonian systems (Libermann and Marle, 1987), but also those Poisson brackets stemming from network representations of physical systems, representing Kirchoff's laws of electrical circuits or the kinematic and static relations mechanisms (Maschke et al., 1992, 1995; Maschke and van der Schaft, 1997) or general interconnection relations on complexes (van der Schaft and Maschke, 2009). For chemical reaction networks or models of CSTRs, the topology of systems is defined by the stoichiometry of the reactions and plays an essential role in the definition of the structure matrices of the (quasi-)Hamiltonian representations (Couenne et al., 2008b; Otero-Muras et al., 2008; Hoang et al., 2011; van der Schaft and Maschke, 2010) and will be detailed in the Section 4 for models of CSTR.

The actual structure matrix $\mathcal{J}$ is modulated by the function R defined in (4) which depends on the differentials of both the Hamiltonian function

$U(x)$ and the entropy function $S(x)$ and has been defined in such a way that the variation of the entropy of the drift dynamics (5) is positive

$$\frac{dS}{dt} = R\frac{\partial S}{\partial x}^{\top} J\frac{\partial U}{\partial x} = \gamma\left(x, \tfrac{\partial U}{\partial x}\right)\{S,U\}_J^2 = \sigma_{int} \geq 0$$

using the assumption that $\gamma\left(x, \frac{\partial U}{\partial x}\right)$ is a positive definite function. For thermodynamic systems this inequality expresses the second law of thermodynamics; the entropy balance of an isolated thermodynamic system is always greater or equal to zero and equal to the *internal entropy production*. Furthermore if the generating function (the Hamiltonian) is chosen as the internal energy, then the entropy is a state variable with gradient $\frac{\partial S}{\partial x}$ being a vector whose elements are either 1 or 0 (Jongschaap and Öttinger, 2004; Favache et al., 2010). Since the Poisson bracket is defined with respect to the constant matrix J, the bracket $\{S,U\}_J$ is a linear combination of the co-energy variables (coefficients of $\frac{\partial U}{\partial x}$) and actually may be interpreted as the *thermodynamic driving force* (see Section 4).

For the complete control system (3), the interaction with the environment is modelled through the vector fields gu and W. The vector field gu is the usual input vector field, where g is the input map and $u(t)$ is the controlled, or time dependent input of the system. The vector field W on other hand models the *uncontrolled* interactions. These interactions may be given by state dependent inputs and outputs like mass flows in chemical reactors where the system undergoes isochore and isobaric transformations. There are two balance equations associated with the control system (3). The first one is associated with the Hamiltonian function $U(x)$

$$\frac{dU}{dt} = \frac{\partial U}{\partial x}^{\top}(W + gu) \tag{7}$$

which express, for physical systems that the variation of energy is solely due to its supply by its environment. The second balance equation is associated with the entropy function $S(x)$

$$\frac{dS}{dt} = R\frac{\partial S}{\partial x}^{\top} J\frac{\partial U}{\partial x} + \frac{\partial S}{\partial x}^{\top} (W + gu) \tag{8}$$

which is now composed by the term of irreversible entropy creation of the internal dynamics of the system and the entropy flow due to the interaction with its environment. Despite that we are restricting our work to a specific class of systems, this class is wide enough to encompass several thermodynamic processes of practical importance, notably chemical reactions and heat exchange processes (Ramirez, 2012) as will be illustrated with the following example.

2.4. Example: the heat exchanger

Consider two simple thermodynamic systems, indexed by 1 and 2 (for instance two ideal gases), which may interact only through a conducting wall. The dynamic of this system is given by the following equation

$$\begin{bmatrix} \dot{S}_1 \\ \dot{S}_2 \end{bmatrix} = \lambda \begin{bmatrix} \frac{T_2(S_2)}{T_1(S_1)} - 1 \\ \frac{T_1(S_1)}{T_2(S_2)} - 1 \end{bmatrix} + \lambda_e \begin{bmatrix} 0 \\ \frac{T_e(t)}{T_2(S_2)} - 1 \end{bmatrix} \tag{9}$$

where S_1 and S_2 (resp. T_1 and T_2) are the entropies (resp. the temperatures) of subsystem 1 and 2, $T_e(t)$ is the time dependent (controlled) temperature of the environment and $\lambda > 0$ (resp. $\lambda_e > 0$) denotes Fourier's heat conduction coefficient of the heat conducting wall between the two compartments (resp. between compartement 2 and the environment). Assuming that the two compartments contain a pure ideal gas and that they undergo no deformation,

and are closed, the temperatures may be modelled as exponential functions of the entropies (Couenne et al., 2006) $T(S_i) = T_0 \exp\left(\frac{S_i}{c_i}\right)$, where T_0 and c_i are constants. This system may be written as

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \end{bmatrix} = \lambda \left(\frac{1}{\frac{\partial U}{\partial x_2}} - \frac{1}{\frac{\partial U}{\partial x_1}} \right) \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} \frac{\partial U}{\partial x_1} \\ \frac{\partial U}{\partial x_2} \end{bmatrix} + \lambda_e \begin{bmatrix} 0 \\ \frac{1}{\frac{\partial U}{\partial x_2}} - \frac{1}{u} \end{bmatrix} u,$$

where $x = [S_1, S_2]$, $U(x_1, x_2) = U_1(x_1) + U_2(x_2)$ is the internal energy of the overall system, sum of the internal energies of each subsystem, $u(t)$ the controlled input that corresponds to the external temperature $T_e(t)$ with $\frac{\partial U}{\partial x_i} = T_i(x_i)$. Rewrite this systems as a IPHS (3) by

$$\dot{x} = R(x, T)JT(x) + W + g(T)u(t), \tag{10}$$

with

$$R(x, T(x)) = \lambda \left(\frac{1}{T_2} - \frac{1}{T_1} \right), \tag{11}$$

$J = \left[\begin{smallmatrix} 0 & -1 \\ 1 & 0 \end{smallmatrix}\right]$ (where, for the sake of keeping a physical interpretation we denote $\frac{\partial U}{\partial x} = T(x) = [T_1(x_1), T_2(x_2)]^T$) and with input map defined by $W = -\lambda_e \left[\begin{smallmatrix} 0 \\ 1 \end{smallmatrix}\right]$ and $g = \frac{\lambda_e}{T_2} \left[\begin{smallmatrix} 0 \\ 1 \end{smallmatrix}\right]$. Let us verify that the system (10) fulfils the Definition 1. The total entropy of the system is given by the sum of the entropies of each compartments $S(x) = x_1 + x_2$. The Poisson bracket $\{S, U\}_J$ is then simply the difference of temperatures between the compartments

$$\{S, U\}_J = \frac{\partial S}{\partial x}^\top J \frac{\partial U}{\partial x} = \begin{bmatrix} 1 \\ 1 \end{bmatrix}^\top \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} T_1 \\ T_2 \end{bmatrix} = T_1 - T_2.$$

It may be noted immediately that the bracket is indeed the driving force of the heat conduction. Then one may identify the expression of the modulating

function (11) with (4) and obtain

$$\gamma = \frac{\lambda}{T_1 T_2}.$$

Since the heat conduction coefficient satisfy $\lambda > 0$, as well as the temperatures $T_1 > 0$ and $T_2 > 0$, then the condition $\gamma > 0$ is also satisfied. The input map $W + g(T)u$ defines entropy flows generated by the interaction of subsystem 2 and the external heat source and depends on the heat conduction coefficient λ_e between them. ■

3. Formulation in the Thermodynamic Phase Space

As has been shown in the Section 2.2, the standard Hamiltonian formulation is not suited for expressing both the first principle (conservation of the total energy) and the second principle (irreversible entropy creation). However there exists an alternative geometric structure to Poisson brackets, namely the contact structure, which appears in an intrinsic way, attached to the geometric formulation of the equilibrium properties of thermodynamic systems by Gibbs (Gibbs, 1873, 1928). The geometric representation of Equilibrium Thermodynamics as sets of tangent planes in the Thermodynamic Phase Space (TPS) constituted of the $n + 1$ extensive and n intensive variables of the system, has been formulated in differential-geometric terms as so-called contact structures (Hermann, 1973; Arnold, 1989; Mrugała, 1978). Reversible transformations have been formulated as contact vector fields (Mrugała, 2000), that has been generalized to irreversible transformations of open thermodynamic systems (Eberard, 2006; Eberard et al., 2007).

In this section we shall first briefly recall the definition of the control systems defined on such contact structures, called conservative contact systems

according to Eberard et al. (2007). It is mainly devoted to the lift of the IPHS (3) to the TPS similarly as it has been suggested in previous work (Eberard et al., 2007; Favache et al., 2010). The specific structure of IPHS is used to suggest an alternative to the previously defined lifts (Eberard et al., 2007; Favache et al., 2010) in order to ensure some additional regularity properties and may be seen as the continuation and a partial answer to the problem of choice of some suitable lifts among all admissible ones (Favache et al., 2009).

3.1. Conservative controlled contact systems

The main definitions and properties of the control contact systems used in this paper are briefly recalled in the sequel; for a detailed presentation of control contact systems the reader is referred to Eberard et al. (2007); Favache (2009); Favache et al. (2009, 2010) and Eberard (2006).

Contact systems are defined on a $(2n+1)$-dimensional state space with $n \in \mathbb{N}^*$ which for simplicity we identify with the real vector space $\mathcal{T} = \mathbb{R}^{2n+1}$. This state space is endowed with a *contact form* θ which, in a set of *canonical coordinates* $(x_0, x, p) \in \mathbb{R} \times \mathbb{R}^n \times \mathbb{R}^n$, is given by

$$\theta = dx_0 - \sum_{i=1}^{n} p_i dx_i,$$

where d denotes the differential operator. The space $\mathcal{T}$ is then called a contact manifold. Associated with the contact form there is a set of distinguished submanifolds, called *Legendre submanifolds*, denoted by $\mathcal{L}$, which are defined by the Pfaffian equation: $\theta = 0$.

Definition 2. *(Libermann and Marle, 1987) A Legendre submanifold of a $(2n+1)$-dimensional contact manifold $(\mathcal{T}, \theta)$ is an n-dimensional integral submanifold $\mathcal{L} \subset \mathcal{T}$ of θ.*

It has been shown in Arnold (1989) that Legendre submanifolds may be described locally by using generating functions. For instance by choosing some real smooth function $U(x)$ the submanifold

$$\mathcal{L}_U = \left\{ x_0 = U(x), x = x, p = \frac{\partial U}{\partial x}(x) \right\} \tag{12}$$

defines indeed a Legendre submanifold.

The relation with Equilibrium Thermodynamics may be illustrated as follows. Consider a mixture of $(n-2)$ species with the extensive variables U, N_i, V, and S, respectively the internal energy, the number of moles of the ith chemical specie, the volume and the entropy, and the intensive variables μ_i, P and T, respectively the chemical potential of the ith chemical specie, the pressure and the temperature of the mixture. Then the Pfaffian equation $\theta = 0$ is nothing else than the statement of Gibbs' relation

$$dU = \sum_{i=1}^{n-2} \mu_i dN_i - PdV + TdS$$

with the identification $x_0 = U$, $x = (N_1, \ldots, N_{n-2}, V, S)$ and $p = (\mu_1, \ldots, \mu_{n-2}, (-P), T)$.

Contact vector fields on a contact manifold are the analogue of Hamiltonian vector fields defined with respect to a symplectic form (Libermann and Marle, 1987). They are uniquely defined by a smooth function called *contact Hamiltonian*. If the contact Hamiltonian function is denoted by K then in a set of canonical coordinates the associated contact vector field X_K is expressed by

$$X_K = \begin{bmatrix} K \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & -p^\top \\ 0 & 0 & -I_n \\ p & I_n & 0 \end{bmatrix} \begin{bmatrix} \frac{\partial K}{\partial x_0} \\ \frac{\partial K}{\partial x} \\ \frac{\partial K}{\partial p} \end{bmatrix}, \tag{13}$$

where I_n denotes the identity matrix of order n. An important property of contact vector fields is whether they leave some Legendre submanifold invariant (defining for instance the equilibrium properties of a system) and may be checked using the following proposition.

Proposition 3. *(Mrugala et al., 1991) Let $\mathcal{L}$ be a Legendre submanifold. Then X_K is tangent to $\mathcal{L}$ if and only if K vanishes on $\mathcal{L}$, i.e., $\mathcal{L} \subset K^{-1}(0)$.*

These vector fields allow to define dynamical systems for thermodynamic processes (Mrugała, 2000) that are the analogue of Hamiltonian systems for mechanical systems. Controlled contact systems have been introduced in Eberard et al. (2005) and used for modelling and analysis of simple and complex open thermodynamic systems (Eberard et al., 2007). They are defined by

$$\frac{dx}{dt} = X_{K_0} + \sum_{i=1}^{m} X_{K_c^i} \tag{14}$$

where $K_0(x_0, x, p) \in C^\infty(\mathcal{T}) \to \mathbb{R}$ is the *internal contact Hamiltonian* that models the internal behaviour of the system, $K_c^i(x_0, x, p, u_i) \in C^\infty(\mathcal{T} \times \mathbb{R}) \to \mathbb{R}$ are the *interaction (or control) contact Hamiltonians* that models the ports of the system and where $X_{K_0^i}$ and X_{K_c} are contact vector fields with respect to the contact form θ.

A *conservative controlled contact system* is defined with respect to a Legendre submanifold in such a way that it leaves this Legendre submanifold invariant (the thermodynamic properties invariant).

Definition 4. *(Eberard et al., 2007) A conservative control contact system is defined as a control contact system (14) with the contact Hamiltonians*

satisfying the invariance condition

$$K_0\big|_{\mathcal{L}} = 0, \quad K_c^i\big|_{\mathcal{L}} = 0,$$

where $\cdot|_{\mathcal{L}}$ *denotes the restriction to* $\mathcal{L}$*.*

3.2. Lift of control systems to the TPS

Models of open irreversible thermodynamic systems are in general expressed in terms of n balance equations which are expressed as the time variation of the n independent extensive variables or any equivalent set of independent dynamic equations in terms of some of the conjugated intensive variables. It may be of interest to use more than only n variables to express the dynamical behaviour of the system and possibly express in terms of dynamic equations of all $(2n+1)$ extensive and intensive variables of the thermodynamic system. This corresponds to lift the n independent balance equations to the complete TPS and may be performed in a systematic way as follows. Let us consider the control system

$$\dot{x} = f\left(x, \tfrac{\partial U}{\partial x}\right) + g\left(x, \tfrac{\partial U}{\partial x}\right) u. \tag{15}$$

Following Eberard et al. (2007); Favache et al. (2009, 2010), this system may be lifted to a control contact system on the TPS by defining the internal contact Hamiltonian function and the control contact functions

$$K_0 = \left(\tfrac{\partial U}{\partial x} - p\right)^\top f\left(x, \tfrac{\partial U}{\partial x}\right); \quad K_c^i = \left(\tfrac{\partial U}{\partial x} - p\right)^\top g_i\left(x, \tfrac{\partial U}{\partial x}\right), \tag{16}$$

if the vector fields defining the control system (15) are all C^∞ on the TPS.

It may be noticed that on the Legendre submanifold $\mathcal{L}_U$ generated by U (defined by (12)), the vector $\left(\frac{\partial U}{\partial x} - p\right)$ vanishes, hence also these contact

Hamiltonian functions vanish and hence the contact vector field leaves invariant the Legendre submanifold where the contact Hamiltonian is zero. Using the expression in local coordinates of the contact vector field (13) one verifies that on the restriction to $\mathcal{L}_U$ the x coordinate satisfies $\dot{x}|_{\mathcal{L}_U} = f\left(x, \frac{\partial U}{\partial x}\right) + g\left(x, \frac{\partial U}{\partial x}\right) u$. The dynamics on the remaining coordinates x_0 and p express equivalent expressions and the reader is referred to Eberard et al. (2007); Favache et al. (2010) for further details.

However, as it has been shown in Favache et al. (2009), there are infinite different possibilities to perform the lift of a dynamical system, each one defined by different contact Hamiltonian functions. One possibility is to define the contact Hamiltonian as

$$K_0 = \left(\frac{\partial U}{\partial x} - p\right)^\top f(x,p); \quad K_c^i = \left(\frac{\partial U}{\partial x} - p\right)^\top g_i(x,p). \tag{17}$$

One may show that again the restriction to the Legendre submanifold $\mathcal{L}_U$ yields the original control system (15) although the contact control systems are different outside the Legendre submanifold. In this case the intensive variables have been "parametrized" by the p coordinates and this might be very useful in order to derive control laws for these contact systems (Ramirez et al., 2011c; Ramirez, 2012). However it appears that the contact Hamiltonian defined in (17) may not be defined on the whole TPS: there might appear singularities often associated to the energy balance equation. This is precisely the case in the original works of Eberard et al. (2007) and Favache et al. (2009, 2010). The lifted contact system is then only well-defined on open submanifolds of the TPS which contain the Legendre submanifold $\mathcal{L}_U$. This is now discussed more in details on the example of the heat exchanger presented in Section 2.4.

3.3. Lift of the model of heat exchanger on the TPS

Recall the model of the heat exchanger (9) which may be expressed as the IPHS (10) with the modulating function being $R(x,T(x)) = \gamma\left(x,T(x)\right)\left\{S,U\right\}_J$ with $\gamma\left(x,T(x)\right) = \frac{\lambda}{T_1(x)T_2(x)}$, $\left\{S,U\right\}_J = T_1\left(x\right) - T_2\left(x\right)$ where we denote $\frac{\partial U}{\partial x} = T(x) = [T_1(x_1), T_2(x_2)]^T$ for the sake of simplicity of notations. Notice that the temperature function is greater than zero for all x which implies that $R(x,T(x))$ is well defined for all x. The input map is defined by $W = -\lambda_e \left[\begin{smallmatrix}0\\1\end{smallmatrix}\right]$ and $g = \frac{\lambda_e}{T_2}\left[\begin{smallmatrix}0\\1\end{smallmatrix}\right]$. The thermodynamic properties of the system are defined by the Legendre submanifold $\mathcal{L}_U$ generated by the total internal energy $U = U_1 + U_2$,

$$\mathcal{L}_U : \left\{ \begin{array}{ll} x_0 & = U \\ x & = [S_1, S_2]^\top \\ p & = \left[\frac{\partial U}{\partial S_1}, \frac{\partial U}{\partial S_2}\right]^\top = [T_1, T_2]^\top \end{array} \right\}. \tag{18}$$

As mentioned before, lifting this system to the TPS may be done in infinite ways. In previous work (Eberard et al., 2007) this lift has been performed by using the contact Hamiltonians (17) with the following parametrization of R and g

$$R(p) = \lambda\left(\frac{1}{p_2} - \frac{1}{p_1}\right) = \lambda\left(\frac{p_1 - p_2}{p_1 p_2}\right), \quad g(p) = \frac{\lambda_e}{p_2}\begin{bmatrix}0\\1\end{bmatrix}. \tag{19}$$

It is immediate that $R(p)$ and $g(p)$ in (19) are undefined when $p_1 = 0$ or $p_2 = 0$. Hence, the lift using the previously defined parametrization is not defined on the whole TPS but only on an open subset which includes the Legendre submanifold $\mathcal{L}_U$: restricted to this submanifold the dynamics in the entropy variables x of the contact control system coincides with the control system (10) (Eberard et al., 2007).

This issue can be overcome by regularizing the contact Hamiltonian functions. Notice that $\gamma = \frac{\lambda}{T_1 T_2}$ admits a singularity at $T_1 = 0$ or $T_2 = 0$ but $\{S, U\}_J = T_1 - T_2$ is a smooth function of the temperatures. The vector field $W = -\lambda_e \left[\begin{smallmatrix} 0 \\ 1 \end{smallmatrix}\right]$ is well-defined but $g = \frac{\lambda_e}{T_2} \left[\begin{smallmatrix} 0 \\ 1 \end{smallmatrix}\right]$ admits a singularity as function of the temperature at $T_2 = 0$. The lift may then be defined alternatively by using the contact Hamiltonians (17) with the following parametrization of R and g

$$R(x,p) = \left(\frac{\lambda}{T_1(x)\, T_2(x)}\right)(p_1 - p_2), \quad g(x) = \frac{\lambda_e}{T_2(x)} \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

Now the contact Hamiltonian functions (17) are defined on the complete TPS as the temperatures are strictly positive functions. This parametrization of R and g generates a different contact vector field than the one defined by (19), but as previously discussed, it is possible to verify using equation (13) that on the restriction to $\mathcal{L}_U$ the dynamics in the entropy variables x coincides with the control system(10). ■

3.4. Regular lift of IPHS to the TPS

We have seen on the example of the heat exchanger that the IPHS (3) may very well be a well-defined control system but the modulating function R admits some singularity, due to the positivity of some intensive variables such as the temperature. In this section we shall suggest an alternative to the lift defined by the contact Hamiltonians (16) which is defined on the complete Thermodynamic Phase Space.

Proposition 5. *The conservative contact system generated by the internal*

contact Hamiltonian function

$$K_0 = -p^\top \gamma\left(x, \tfrac{\partial U}{\partial x}\right)\left(\frac{\partial S}{\partial x}^\top Jp\right) J\frac{\partial U}{\partial x} + \left(\tfrac{\partial U}{\partial x} - p\right)^\top W\left(x, \tfrac{\partial U}{\partial x}\right) \qquad (20)$$

and control Hamiltonian functions

$$K_c^i = \left(\tfrac{\partial U}{\partial x} - p\right)^\top g_i\left(x, \tfrac{\partial U}{\partial x}\right) \qquad (21)$$

is a lift of the IPHS of Definition 1 leaving invariant the Legendre submanifold $\mathcal{L}_U$ and defined on the complete Thermodynamic Phase Space.

Indeed as the functions $S(x)$ and $U(x)$ are assumed to be C^∞ real functions on the space $\mathbb{R}^n$, the contact Hamiltonian functions are all C^∞ real functions on the TPS $\mathbb{R}^{2n+1}$. Furthermore the contact Hamiltonian functions (20) and (21) vanish on the Legendre submanifold $\mathcal{L}_U$ generated by $U(x)$. Hence they define a conservative control contact system with respect to the Legendre submanifold $\mathcal{L}_U$.

According to (13) and noticing that none of the contact Hamiltonians depend on x_0, the internal contact Hamiltonian function (20) generates the contact vector field

$$X_{K_0} = \begin{bmatrix} \bar{\gamma}(x)\left(\frac{\partial S}{\partial x}^\top Jp\right)\left(p^\top J\frac{\partial U}{\partial x}\right) + \frac{\partial U}{\partial x}(x)^\top \bar{W}(x) \\ \bar{\gamma}(x)\ J\ \left[\left(\frac{\partial U}{\partial x}^\top Jp\right)\frac{\partial S}{\partial x} + \left(\frac{\partial S}{\partial x}^\top Jp\right)\frac{\partial U}{\partial x}\right] + \bar{W}(x) \\ \left[-\left(p^\top J\frac{\partial U}{\partial x}(x)\right)\frac{\partial}{\partial x}\left[\bar{\gamma}(x)\left(\frac{\partial S}{\partial x}^\top Jp\right)\right] + ... \right. \\ ... + \bar{\gamma}(x)\left(\frac{\partial S}{\partial x}^\top Jp\right)\frac{\partial^2 U}{\partial x^2}(x)Jp + ... \\ \left. ... + \left(\frac{\partial U}{\partial x}(x) - p\right)^\top \frac{\partial \bar{W}}{\partial x}(x) + \frac{\partial^2 U}{\partial x^2}(x)\bar{W}(x)\right] \end{bmatrix}$$

where we denote the function $\gamma\left(x, \frac{\partial U}{\partial x}\right) = \bar{\gamma}(x)$ and the vector field $W\left(x, \frac{\partial U}{\partial x}\right) = \bar{W}(x)$ for the sake of notational simplicity. The control contact Hamiltonian

functions (21) generate the following contact vector field

$$X_{K_c^i} = \begin{bmatrix} \frac{\partial U}{\partial x}(x)^\top g(x) \\ g(x) \\ \frac{\partial^2 U}{\partial x^2}(x) g(x) \end{bmatrix}.$$

When restricting these conservative contact vector fields to the Legendre submanifold $\mathcal{L}_U$ (where $p = \frac{\partial U}{\partial x}(x)$), one notice immediately that the control contact vector field $X_{K_c^i}$ keeps its expression but the restriction of the drift contact vector field X_{K_0} may be expressed as

$$X_{K_0}|_{\mathcal{L}_U} = \begin{bmatrix} \frac{\partial U}{\partial x}(x)^\top \bar{W}(x) \\ \bar{\gamma}(x)\ J\left(\frac{\partial S}{\partial x}^\top J p\right) \frac{\partial U}{\partial x} + \bar{W}(x) \\ \bar{\gamma}(x) \left(\frac{\partial S}{\partial x}^\top J p\right) \frac{\partial^2 U}{\partial x^2}(x) J p + \frac{\partial^2 U}{\partial x^2}(x) \bar{W}(x) \end{bmatrix}.$$

As both contact Hamiltonians vanish on the Legendre submanifold $\mathcal{L}_U$, the latter is invariant and the lifted IPHS restricted to it, $\frac{d}{dt}\left([x_0, x, p]^\top\right)\big|_{\mathcal{L}_U} = X_{K_0} + \sum_{i=1}^m X_{K_c^i}\big|_{\mathcal{L}_U}$, may be written as

$$\begin{aligned} \frac{dx_0}{dt}\Big|_{\mathcal{L}_U} &= \frac{dU}{dt} = \frac{\partial U}{\partial x}^\top(x) W\left(x, \frac{\partial U}{\partial x}\right) + \frac{\partial U}{\partial x}^\top(x) g u, \\ \frac{dx}{dt}\Big|_{\mathcal{L}_U} &= R\left(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x}\right) J \frac{\partial U}{\partial x}(x) + W\left(x, \frac{\partial U}{\partial x}\right) + g u, \\ \frac{dp}{dt}\Big|_{\mathcal{L}_U} &= \frac{\partial^2 U}{\partial x^2}\left(R\left(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x}\right) J \frac{\partial U}{\partial x}(x) + W\left(x, \frac{\partial U}{\partial x}\right) + g u\right), \end{aligned} \tag{22}$$

and may be interpreted as follows. On the second line, one recovers indeed the IPHS (3) hence the lifted conservative control system defined by Proposition 5 indeed embeds the balance equations defining the IPHS. The first line expresses the energy balance equation (7). Finally the third line gives the equivalent expression of the IPHS in the intensive variables.

Let us now compare this lift with the canonical lift defined by the internal and control contact Hamiltonian functions (16) for the IPHS of Definition 1.

In order to keep the notation brief we shall denote

$$\bar{R}(x) = R\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}\right) = \bar{\gamma}(x)\left(\frac{\partial S}{\partial x}^{\top} J \frac{\partial U}{\partial x}\right)$$

According to (16) the IPHS is lifted to the conservative contact control systems defined by the the internal contact Hamiltonian function

$$K_0(x_0, x, p) = -p^{\top}\bar{R}(x) J \frac{\partial U}{\partial x}(x) + \left(\tfrac{\partial U}{\partial x} - p\right)^{\top} W\left(x, \tfrac{\partial U}{\partial x}\right) \tag{23}$$

and control contact Hamiltonian function

$$K_c^i(x_0, x, p) = \left(\tfrac{\partial U}{\partial x} - p\right)^{\top} g\left(x, \tfrac{\partial U}{\partial x}\right). \tag{24}$$

Note that the contact Hamiltonians are smooth and well defined in the whole TPS and generate the following conservative contact vector field

$$X_{K_0+\sum_{i=1}^m X_{K_c^i} u_i} = \begin{bmatrix} \frac{\partial U}{\partial x}(x)^{\top}\left[W\left(x, \frac{\partial U}{\partial x}\right) + g\left(x, \frac{\partial U}{\partial x}\right)\right] \\ \bar{R}(x) J \frac{\partial U}{\partial x}(x) + W\left(x, \frac{\partial U}{\partial x}\right) + g\left(x, \frac{\partial U}{\partial x}\right) \\ \left[-\frac{\partial \bar{R}}{\partial x}(x) p^{\top} J \frac{\partial U}{\partial x}(x) + \bar{R}(x) \frac{\partial^2 U}{\partial x^2}(x) J p + ... \right. \\ \left. ... + \left(\frac{\partial U}{\partial x} - p\right)^{\top} \frac{\partial}{\partial x} g\left(x, \frac{\partial U}{\partial x}\right) + \frac{\partial^2 U}{\partial x^2}(x) g\left(x, \frac{\partial U}{\partial x}\right)\right] \end{bmatrix}$$

When restricted to the the Legendre submanifold $\mathcal{L}_U$ (where $p = \frac{\partial U}{\partial x}(x)$), this vector field generates again the system (22) which is again the IPHS expressed on the Legendre submanifold. Notice that the contact vector fields are different *outside* the Legendre submanifold. Finally let us remark that while the lift of Proposition 5 leads to a conservative control contact system defined on the whole TPS there might be other possible regularizing functions of $\gamma(x, p)$, as a partially parametrized function $\tilde{\gamma}\left(x, \frac{\partial U}{\partial x}, p\right)$, leading to other possible lifts among all possible ones (Favache et al., 2009). This might be very desirable for the aim of control design (Ramirez et al., 2011b,a) and actually will be illustrated in the next section.

4. On the Hamiltonian formulation of the CSTR

In this section we present the IPHS representation of a continuous stirred tank reactor (CSTR) model (assuming constant volume and pressure in the reactor) and considering that a single reaction with arbitrary stoichiometry takes place.

In a first paragraph we remind three different quasi-Hamiltonian formulations of the mass and energy or entropy balance equations describing the CSTR with Hamiltonian functions being the either the entropy, the internal energy or the enthalpy. We show that the structure matrices suffers the same drawbacks than in the example of heat transfer in Section 2.4, namely that the structure matrices depend on the gradient of the Hamiltonian and hence do not define a true Hamiltonian system.

In the second paragraph we suggest a IPHS formulation of the CSTR dynamics according the Definition 1 for which the Hamiltonian is the internal energy, the constant skew-symetric matrix is constant and defined by the stoichiometric coefficients uniquely (Proposition 6).

In the third paragraph, this IPHS representation is lifted to the associated Thermodynamic Phase Space in two ways, the first one defined according to the Proposition 5 and the second one being an alternative using the specific definition of the modulating function.

4.1. Reminder on alternative formulations of the CSTR dynamics

We recall briefly the notation and the balance equations describing the dynamic of the CSTR.

4.1.1. The mass balance equations

Assume a chemical reaction in a CSTR with the following reversible reaction scheme

$$\nu_1 A_1 + \ldots + \nu_l A_l \rightleftharpoons \nu_{l+1} A_{l+1} + \ldots + \nu_m A_m, \qquad m > l \geq 1.$$

The time variation of the species in the reactor is given by (Aris, 1989)

$$\dot{n}_i = F_{ei} - F_{si} + r_i V \qquad i = 1, \ldots, m \tag{25}$$

where n_i is the number of moles of the species i, (and $\mathbf{n}$ the vector $\mathbf{n} = (n_1, \ldots, n_m)^\top$), F_{ei} and F_{si} are respectively the inlet and outlet molar flows (and $\mathbf{F}_e$ the vector $\mathbf{F}_e = (F_{e1}, \ldots, F_{em})^\top$), $r_i = \bar{\nu}_i r$ where $r(\mathbf{n}, T)$ is the reaction rate which is the difference of the forward reaction rate r_f and the backward reaction rate r_b: $r = (r_f - r_b)$ and depends on the temperature and on the reactant mole number, $\bar{\nu}_i$ is the signed stoichiometric coefficient: $\bar{\nu}_i = -\nu_i$ if it appears on the left hand side of the reaction scheme, $\bar{\nu}_i = \nu_i$ in the other case. Following the usual assumptions (Aris, 1989; Favache and Dochain, 2009), V the volume in the reactor is assumed to be constant as well as the pressure. We shall assume a reaction in gas phase, but the developments may be applied identically to a reactor with a reaction in liquid phase. The assumptions of constant volume and pressure impose a constraint over the total outlet flow $F_s(\mathbf{n}, T, \mathbf{F}_e)$ as discussed in (Couenne et al., 2006, 2008b), making the outlet flows $F_{si} = y_i F_s$ state dependent with $y_i = \frac{n_i}{\sum_{j=1}^{m} n_i}$ being the molar fraction of the species i.

4.1.2. The energy and entropy balance equations

The classical construction of the state space of the ideal mixture in the CSTR is based on Gibbs' relation. Assuming constant volume and pressure

of the mixture in the reactor, Gibbs' relation reduces to

$$dU = \sum_{i=1}^{m} \frac{\partial U}{\partial n_i} dn_i + \frac{\partial U}{\partial S} dS \tag{26}$$

where U denotes the internal energy, S the entropy and the conjugated intensive variables are the chemical potential $\frac{\partial U}{\partial n_i} = \mu_i$ and the temperature $\frac{\partial U}{\partial S} = T$. Gibbs' relation can also be written in the so called entropy formulation

$$dS = \sum_{i=1}^{m} \frac{\partial S}{\partial n_i} dn_i + \frac{\partial S}{\partial U} dU \tag{27}$$

where $\frac{\partial S}{\partial n_i} = -\frac{\mu_i}{T}$ and $\frac{\partial S}{\partial U} = \frac{1}{T}$ are the intensive thermodynamic variables conjugated to n_i and the internal energy U. Under the previous assumptions the internal energy of the CSTR is given by

$$U = \sum_{i=1}^{m} n_i [c_{pi}(T - T_0) + u_{0i}], \tag{28}$$

where c_{pi}, u_{0i}, T_0 are respectively the heat capacity at constant pressure, reference molar energy and reference temperature. Assuming constant volume and pressure the reference molar enthalpy $h_{0i} = u_{0i}$ (Sandler, 2006), and the balance equation of the internal energy is (Couenne et al., 2006; Favache and Dochain, 2009)

$$\dot{U} = \dot{H} = \sum_{i=1}^{m} (F_{ei} h_{ei} - F_{si} h_{si}) + Q, \tag{29}$$

where $Q = \lambda(T_e - T)$ is the heat flux from the jacket with λ the heat conduction coefficient, T_e the temperature of the jacket, H the total enthalpy of the reactor and h_{ei}, h_{si} respectively the inlet and outlet specific molar enthalpies, which are related with the chemical potentials and the specific molar entropies s_i by (Couenne et al., 2006)

$$\mu_i = h_i - T s_i.$$

The entropy function of the CSTR is given by

$$S = \mathcal{C}_p \ln\left(\frac{T}{T_0}\right) - R_g \sum_{i=1}^{m} \left[n_i \ln\left(\frac{n_i}{N}\right)\right] + \sum_{i=1}^{m} (n_i s_{0i}), \tag{30}$$

where $\mathcal{C}_p = \sum_{i=1}^{m} n_i c_{pi}$, T_0, N, s_{0i} and R_g are respectively total heat capacity at constant pressure, reference temperature, total number of moles, reference molar entropy and the ideal gas constant. Hence, the entropy balance equation may be deduced from this expression or from Gibbs' relation and is given by

$$\dot{S} = \sum_{i=1}^{m} (F_{ei} s_{ei} - F_s s_i) + \frac{Q}{T_e} + \sigma, \tag{31}$$

where σ is the irreversible entropy creation due to mass transfer, heat transfer and chemical reactions:

$$\sigma = \sum_{i=1}^{m} \frac{F_{ei}}{T}(h_{ei} - T s_{ei} - \mu_i) + \frac{Q}{T} - \frac{Q}{T_e} - \sum_{i=1}^{m} \mu_i \nu_i \frac{r}{T}.$$

4.1.3. Alternative formulations of the CSTR dynamics

In this paragraph we shall recall some alternative formulations for the dynamic of the CSTR as a quasi-port Hamiltonian system in the form:

$$\dot{x} = \Theta\left(x, \frac{\partial \mathcal{H}}{\partial x}\right) \frac{\partial \mathcal{H}}{\partial x}(x) + g\left(\frac{\partial \mathcal{H}}{\partial x}\right) u \tag{32}$$

where $\mathcal{H}(x)$ is the *generating function* (a thermodynamic potential), $\Theta\left(x, \frac{\partial \mathcal{H}}{\partial x}\right)$ is a matrix which is a function of the state variables and the gradient of the generating function, and $g(x)$ is the input map. In the general case, the manipulated input in the CSTR is the heat flux from the jacket $Q = \lambda(T_e - T)$, where T_e is the temperature of the jacket while the input flows of matter are supposed to be constant. The choice of the generating function $\mathcal{H}$ and the matrix Θ for the CSTR model, has been the matter of several papers on its

port Hamiltonian formulations (Sira-Ramírez and Angulo-Nunez, 1997; Hangos et al., 2001; Otero-Muras et al., 2008; Ramirez et al., 2009; Hoang et al., 2011) and it may be noted that, admitting non positive symmetric matrices may lead also to pseudo-Riemannian (Smale, 1972) (also called Brayton-Moser's) formulation Favache and Dochain (2010). In the following we will present some quasi-port Hamiltonian representations that use as generating function a thermodynamic potential: the entropy, the internal energy and the enthalpy functions whose gradient is equal to the generating forces of the thermodynamic process. We refer in particular to Ramirez et al. (2010); Favache et al. (2011); Hoang et al. (2011) where different variations of this representations may be found.

Let us in a first instance consider the following state vector of extensive variables $x_1 = [n_1, \ldots, n_m, U]^\top = [\mathbf{n}^\top, U]^\top$ where the energy balance equation (29) appears as one of the state equations and the entropy function $S(\mathbf{n}, U)$ is used as generating function. Its gradient is then $\frac{\partial S}{\partial x_1} = \left[\left(-\frac{\mu_1}{T}\right), \ldots, \left(-\frac{\mu_m}{T}\right), \frac{1}{T}\right]^\top$. Define the two following skew-symmetric, respectively symmetric structure matrices:

$$\mathcal{J}_f = \begin{bmatrix} 0 & 0 & 0 & f_{n1} \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & f_{nm} \\ -f_{n1} & \ldots & -f_{nm} & 0 \end{bmatrix}, \; M = \begin{bmatrix} 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 \\ 0 & \ldots & 0 & 1 \end{bmatrix} \tag{33}$$

with $f_{ni} = F_{ei} - F_{si}(\mathbf{n}, T) + V\bar{\nu}_i r(\mathbf{n}, T)$. Then define the function

$$\eta_1\left(\mathbf{n}, \frac{\boldsymbol{\mu}}{T}, \frac{1}{T}\right) = T\sum_{i=1}^{m}\left(F_{ei}s_{ei} - F_{si}s_i - \frac{\mu_i}{T}\bar{\nu}_i r(\mathbf{n}, T)\, V\right), \tag{34}$$

where the inverse of the temperature $\frac{1}{T}$ and $\frac{\boldsymbol{\mu}}{T}$ are co-state variables (com-

ponents of the gradient of the entropy function); they are functions of the states $[\mathbf{n}^\top, U]^\top$, derived using Gibbs' relation (27). The inlet flow $\mathbf{F}_e$ as well as the specific entropy s_{ei} at the inlet are assumed to be constant. The mass balance equations (25) and the energy balance equation (29) of the CSTR may then be formulated as the control system (32) with generating function $\mathcal{H} = S$, structure matrix

$$\Theta_1\left(x_1,\, \frac{\partial S}{\partial x_1}\right) = \frac{1}{T}\left(\mathcal{J}_f(x_1,\, T) + \eta_1\left(x_1,\, \frac{\partial S}{\partial x_1}\right) M\right)$$

and input vector $g = \frac{1}{T} g_0$ with $g_0 = [0, \ldots, 0, 1]^\top$ of dimension $m + 1$.

Secondly let us consider the following state vector of extensive variables $x_2 = [n_1, \ldots, n_m, S]^\top = [\mathbf{n}^\top, S]^\top$, where the entropy balance equation (31) appears as one of the state equations and the internal energy $U(\mathbf{n}, S)$ is used as generating function. Its gradient is then $\frac{\partial U}{\partial x_2} = [\mu_1, \ldots, \mu_m, T]^\top$. Define the function

$$\eta_2(\mathbf{n}, S, T) = \frac{1}{T}\sum_{i=1}^{m}(F_{ei} h_{ei} - F_{si} h_{si})$$

where now the temperature T and the specific enthalpy h_i are considered as functions of the state $[\mathbf{n}^\top, S]^\top$ and are derived using Gibbs' relation (26). The mass balance equations (25) and the energy balance equation (31) of the CSTR may then be formulated as the control system (32) with generating function $\mathcal{H} = U$, structure matrix

$$\Theta_2\left(x_2,\, \frac{\partial U}{\partial x_2}\right) = T\left(\mathcal{J}_f(x_2,\, T) + \eta_2(x_2,\, T)\, M\right). \tag{35}$$

and input vector $g_0 = [0, \ldots, 0, 1]^\top$ of dimension $m + 1$.

It is possible to obtain **a third formulation by considering the state vector** $x_3 = [n_1, \ldots, n_m, T]^\top = [\mathbf{n}^\top, T]^\top$. In this case the energy balance

equation (29) is expressed as a state equation of the temperature and the generating function is the total enthalpy H, the Legendre transformation with respect to the entropy of the internal energy U. The total enthalpy is given by

$$H = \sum_{i=1}^{m} n_i h_i(T) \tag{36}$$

under the assumption of constant volume and pressure. Denoting $\mathcal{C}_p(n) = \frac{\partial H}{\partial T}$ and $c_{pi} = \frac{\partial h_i}{\partial T}$, hence $\mathcal{C}_p(n) = \sum_{i=1}^{m} n_i c_{pi}$, its gradient is

$$\frac{\partial H}{\partial x} = [h_1(T), \ldots, h_m(T), \mathcal{C}_p(n)]^\top.$$

The energy balance equation (29) may then be written in terms of the temperature as follows:

$$\mathcal{C}_p \frac{dT}{dt} = \sum_{i=1}^{m} F_{ei} c_{pi}(T - T_0) - \sum_{i=1}^{m} h_i r_i V + Q. \tag{37}$$

Define the function

$$\eta_3(\mathbf{n},\, T,\, \mathbf{h}) = \frac{1}{\mathcal{C}_p} \sum_{i=1}^{m} (F_{ei} h_{ei} - F_{si} h_i)$$

where now the specific enthalpy $h_i(T)$ and the outlet flows F_{si} are considered as functions of the state $[\mathbf{n}^\top, T]^\top$. The mass balance equations (25) and the energy balance equation (29) of the CSTR may now be formulated as the control system (32) with generating function $\mathcal{H} = H$, structure matrix

$$\Theta_3\left(x_3,\, \frac{\partial H}{\partial x_{23}}\right) = \frac{1}{\mathcal{C}_p} \left(\mathcal{J}_f(x_3) + \eta_3(x_3,\, \mathbf{h})\, M\right)$$

and input vector $g = \frac{1}{\mathcal{C}_p} g_0$ with $g_0 = [0, \ldots, 0, 1]^\top$ of dimension $m + 1$.

As a conclusion, let us notice that although the three formulations seem to have a structured form in terms of system (32), this structure does actually not reveal the conservation of energy and irreversible entropy creation.

Indeed the structure matrices were constructed ad hoc from the chosen expressions of the energy or entropy balance equations and not clearly related to the topology of the system defined by the stoichiometry of the reaction (Oster and Perelson, 1974). One may observe that the second and third formulations have both a conserved quantity (the internal energy and the enthalpy) as generating function but both admit a symmetric part ηM in the structure matrix Θ! Only the first formulation with the entropy as generating function, justifies the symmetric part of the structure matrix. Additionally from the definition of the structure matrices, it appears immediately that they are all actually defined in terms of the co-state variables, the gradient of the generating functions and hence the quasi-port Hamiltonian formulation suffers the same criticism as developed in the Section 2.2.

4.2. IPHS formulation of the CTSR

In this subsection we shall express the dynamics of the CSTR as an IPHS according to Definition 1. The structure matrix will not be constructed ad hoc as in the preceding subsection but strictly represent the stoichiometry of the reaction, the actual topology of the chemical reaction networks. The generating function is chosen to be the energy, a conserved quantity. Finally the expression of the second principle is introduced by the modulating function, depending explicitly on the entropy function. Finally we shall consider as input variables: the heat flow from the jacket Q and the inlet and output molar flows of each specie, F_{ei} and F_{si} respectively.

Proposition 6. *The dynamical equation of the CSTR may be expressed as*

the IPHS (3)

$$\dot{x} = R\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}\right) J \frac{\partial U}{\partial x}(x) + W(x, F_e) + g\frac{Q}{T}* \tag{38}$$

with state vector $x = [n_1, \ldots, n_m, S]^\top$*, the internal energy* $U(x)$ *as Hamiltonian function, the constant skew-symmetric structure matrix*

$$J = \begin{bmatrix} 0 & \ldots & 0 & \bar{\nu}_1 \\ 0 & \ldots & 0 & \vdots \\ 0 & \ldots & 0 & \bar{\nu}_m \\ -\bar{\nu}_1 & \ldots & -\bar{\nu}_m & 0 \end{bmatrix}$$

whose elements are the stoichiometric coefficients of the chemical reaction, and modulating function (4) defined by the product of the positive function

$$\gamma = \frac{rV}{T\mathcal{A}}$$

with the bracket $\{S, U\}_J = -\sum_{i=1}^{m} \bar{\nu}_i \mu_i = \mathcal{A}$*, equal to the chemical affinity of the reaction, the driving force of the chemical reaction. The port of the IPHS is given by* $W + gQ$ *and is composed by the extended input and output flow vector and the thermal interaction vector defined respectively as*

$$W = \begin{bmatrix} F_{e1} - F_{s2} \\ \vdots \\ F_{em} - F_{sm} \\ \omega \end{bmatrix}, \qquad g = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix} \frac{Q}{T} \tag{39}$$

with $\omega = \frac{1}{T}\sum_{i=1}^{m}(F_{ei}s_{ei} - F_{si}s_i)$*.*

Proof. Let us analyse (38) in the sense of Definition 1. As previously mentioned J is constant and skew-symmetric, moreover, it represents the chemical reaction network. It is interesting that the bracket $\{S, U\}_J$ is exactly the

thermodynamic driving force of the chemical reaction. Indeed

$$\{S,U\}_J = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix}^\top \begin{bmatrix} 0 & \dots & 0 & \bar{\nu}_1 \\ 0 & \dots & 0 & \vdots \\ 0 & \dots & 0 & \bar{\nu}_m \\ -\bar{\nu}_1 & \dots & -\bar{\nu}_m & 0 \end{bmatrix} \begin{bmatrix} \mu_1 \\ \vdots \\ \mu_m \\ T \end{bmatrix} = -\sum_{i=1}^{m} \bar{\nu}_i \mu_i = \mathcal{A}.$$

Here $\mathcal{A}$ is the chemical affinity (Kondepudi and Prigogine, 1998), that corresponds to the thermodynamic driving force of the chemical reaction. From the expression of the previous bracket , we have that

$$R = \gamma\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}\right)\{S,U\}_J = \gamma\left(x, \tfrac{\partial U}{\partial x}\right)\mathcal{A},$$

and considering the mass and entropy balance equations, we are lead to define the modulating function as

$$\gamma = \frac{rV}{T\mathcal{A}}. \tag{40}$$

It remains to show that the function γ is a well defined positive definite function. Indeed, from De Donder's fundamental equation (Prigogine and Defay, 1954)

$$\sigma_r = \frac{rV}{T}\mathcal{A} \geq 0, \tag{41}$$

with σ_r the entropy creation due to the chemical reaction and $\sigma_r > 0$ if $\mathcal{A} \neq 0$. Hence for $\mathcal{A} \neq 0$, one has $\gamma = \frac{\sigma_r}{\mathcal{A}^2}$ which relates indeed the function γ to the irreversible entropy production due to the chemical reaction process and makes it a positive function. Remains to show that the function γ is well-defined when $\mathcal{A} = r = 0$ (the only possible singularity since $T > 0$). Therefore recall that the affinity may be decomposed into a forward affinity and a reverse affinity (Oster and Perelson, 1974; Couenne et al., 2006, 2008a)

$$\mathcal{A} = \mathcal{A}_f - \mathcal{A}_r \tag{42}$$

with

$$\mathcal{A}_f = \sum_{i=1}^{l} \nu_i \mu_i \quad \text{and} \quad \mathcal{A}_r = -\sum_{i=l+1}^{m} \nu_i \mu_i \tag{43}$$

and the reaction rate may expressed in terms of the forward and reverse affinities as

$$r(\mathcal{A}_f, \mathcal{A}_r, T) = k_f(T) e^{\frac{\mathcal{A}_f}{R_g T}} - k_r(T) e^{\frac{\mathcal{A}_r}{R_g T}} \tag{44}$$

where $k_f(T)$ and $k_r(T)$ are positive functions depending solely on the temperature and R_g denotes the constant of perfect gas. Using these relations it is possible to rewrite γ in terms of the forward and reverse affinities

$$\gamma = \frac{V}{T} \frac{k_f e^{\frac{\mathcal{A}_f}{R_g T}} - k_r e^{\frac{\mathcal{A}_r}{R_g T}}}{\mathcal{A}_f - \mathcal{A}_r}. \tag{45}$$

To verify that γ is well defined we study its limit when $\mathcal{A} = 0$, i.e., when $\mathcal{A}_f = \mathcal{A}_r$. We may study this limit applying l'Hôpital's rule

$$\lim_{\mathcal{A}_f \to \mathcal{A}_r} \frac{V}{T} \frac{k_f e^{\frac{\mathcal{A}_f}{R_g T}} - k_r e^{\frac{\mathcal{A}_r}{R_g T}}}{\mathcal{A}_f - \mathcal{A}_r} = \frac{V}{R_g T^2} k_f e^{\frac{\mathcal{A}_f}{R_g T}} = \frac{V}{R_g T^2} k_r e^{\frac{\mathcal{A}_r}{R_g T}}, \tag{46}$$

which is well defined since $R_g, T > 0$.

To complete the analysis of (38) it just remains to check that the vectors W and $\frac{1}{T} gQ$ corresponds to input/output ports. The elements of the vector W are composed of the inlet and outlet flows of matter. For the coordinates modelling mass balance they are just the ratio of mass exchange with the environment. Similarly, the element corresponding to the last coordinate represents the ratio of entropy exchange due to mass transfer with the environment. Hence, W is the input/output port related with mass transfer of the IPHS. If the CSTR is connected with another CSTR (as for reactors in series) the connection is performed through this port. The vector $\frac{1}{T} gQ$ has

only the element corresponding to the entropy balance different from zero. This element models the interaction of the reactor with the cooling jacket and represents the entropy flow due to the temperature difference between the reactor and the jacket. Hence the vector $\frac{1}{T}gQ$ is the input/output port related with the thermal interaction not due to mass transfer. □

4.3. Lift of the IPHS

In this section we shall suggest some lift of the IPHS associated with the CSTR model and defined in Proposition 6 to the TPS according to the Section 3.4 and show that for the particular case of the CSTR we may suggest some alternative lifts. The thermodynamic properties of the mixture in the reactor (with assumption of constant volume and pressure) may be defined by the Legendre submanifold of the TPS $\mathbb{R}^{2n+1} \ni (x_0, x, p)$, generated by the internal energy function $U(\mathbf{n}, S)$

$$\mathcal{L}_U : \begin{cases} x_0 = U(\mathbf{n}, S) \\ x = [\mathbf{n}, S]^\top \\ p = [\boldsymbol{\mu}(\mathbf{n}, S), T(\mathbf{n}, S)]^\top \end{cases} \tag{47}$$

A regular lift to a conservative contact control system may be defined according to the procedure discussed in Section 3 but an alternative lift is also defined in the following proposition.

Proposition 7. *A well defined lift of the IPHS formulation of the CSTR as conservative contact control system with respect to the Legendre submanifold*

$\mathcal{L}_U$ defined in (47) is generated by the contact Hamiltonian

$$K = \underbrace{-p^\top R_e\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}, p\right) J \frac{\partial U}{\partial x}(x) + \left(\frac{\partial U}{\partial x} - p\right)^\top W\left(x, \tfrac{\partial U}{\partial x}, p\right)}_{K_0} + \underbrace{\left(\frac{\partial U}{\partial x} - p\right)^\top g \frac{Q}{T}}_{K_c}, \quad (48)$$

with R_e defined either by

$$R_e\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}, p\right) = \frac{r(\mathcal{A}_f(p), \mathcal{A}_r(p), T)V}{T(x)\mathcal{A}(p)}\mathcal{A}(p) \quad (49)$$

or by

$$R_e\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}, p\right) = \frac{r(\mathcal{A}_f(\boldsymbol{\mu}), \mathcal{A}_r(\boldsymbol{\mu}), T)V}{T(x)\mathcal{A}\left(\frac{\partial U}{\partial x}\right)}\mathcal{A}(p). \quad (50)$$

and the vector field

$$W\left(x, \tfrac{\partial U}{\partial x}\right) = \begin{bmatrix} F_{e1} - F_{s2}\left(x, \frac{\partial U}{\partial x}\right) \\ \vdots \\ F_{em} - F_{sm}\left(x, \frac{\partial U}{\partial x}\right) \\ \omega\left(x, \frac{\partial U}{\partial x}\right) \end{bmatrix},$$

where $\omega\left(x, \frac{\partial U}{\partial x}\right) = \frac{1}{T}\sum_{i=1}^m \left(F_{ei}s_{ei} - F_{si}\left(x, \frac{\partial U}{\partial x}\right) s_i\left(x, \frac{\partial U}{\partial x}\right)\right)$.

Notice firstly that when the function R_e is defined as in (50) then the lift is precisely the one given in the Proposition 5. Secondly, when the function R_e is defined as in (49) it is also well-defined on the whole TPS. Indeed from the definition of the forward and reverse affinities in (43), these function are linear functions of the intensive variables and may be extended to linear functions of the co-state p on the TPS: $\mathcal{A}_f(p) = \sum_{i=1}^l \nu_i p_{\mu_i}$ and $\mathcal{A}_r(p) = -\sum_{i=l+1}^m \nu_i p_{\mu_i}$.

And adapting the proof of the definition of the function γ in Proposition 6, it is shown that the function $\frac{r(\mathcal{A}_f(p),\mathcal{A}_r(p),T)V}{T(x)\mathcal{A}(p)}$ is well defined on the whole TPS.

Finally note that while the Hamiltonian of the IPHS representation of the CSTR, the internal energy, has the dimension of energy, the contact Hamiltonian has the dimension of power. Hence K defines a kind of virtual power as it has already been addressed in Eberard et al. (2007). Thanks to the underlying irreversible port Hamiltonian structure of the lift we may easily identify three different power products in (48): two in K_0 and one in K_c, that represent respectively the power contribution due to the chemical reaction, the inlet and outlet flows and the heat transfer through the jacket. The first term in K_0 represents the power contribution of the chemical reaction and is related with the pseudo-Poisson bracket of the IPHS. The second term in K_0:

$$\sum_{i=1}^{m} \left(\mu_i - p_i\right) \left(F_{ei} - F_{si}\left(x, \tfrac{\partial U}{\partial x}\right)\right)$$

is the power generated by the mass exchange between the reactor and its environment; and finally the term

$$\left(T - p_S\right) \left(\sum_{i=1}^{m} \left(F_{ei} s_{ei} - F_{si}\left(x,p\right) s_i\left(x, \tfrac{\partial U}{\partial x}\right)\right) + \frac{Q}{T} \right)$$

represents the power generated by the energy exchange.

5. Conclusion

In the first part of the paper, we have suggested a class of quasi-Hamiltonian system, called *Irreversible Port Hamiltonian System* which is adapted to the representation of (open) irreversible thermodynamic processes. In a very similar manner as for GENERIC (Mushik et al., 2000; Grmela, 2002), they are

defined by two functions: one generating function, the Hamiltonian function, whose gradient defines the generating forces of the irreversible processes and one entropy function. Furthermore they are defined with respect to a structure matrix composed of the product of a constant skew-symmetric structure matrix J (corresponding to a Poisson bracket $\{\ ,\ \}_J$) with a modulating function R which depend as well of the state as the co-state variables. This modulating function itself is the product of some positive function γ and the Poisson bracket $\{S, U\}_J$ of the entropy and the energy function. This construction guarantees that the Hamiltonian function is a conserved quantity and simultaneously that the entropy function satisfies a balance equation containing an irreversible entropy creation term which furthermore vanishes when the gradient of the Hamiltonian (the vector of generating forces) is zero.

In this way the necessary dependence on the co-state variables of any quasi-Hamiltonian representation of irreversible thermodynamic processes has been formulated precisely in terms of this modulating function depending on the state and co-state of the system. In the case of a 2-compartment heat exchanger and a CSTR, these system found a striking physical interpretation. The Hamiltonian being chosen to be the internal energy, the entropy function equal to the total entropy of the system, the constant skew-symmetric matrix is uniquely defined by the stoichiometric coefficients of the reaction in the CSTR and the topology of the heat flows. Furthermore the bracket between the entropy and the energy function is precisely equal to the driving forces of the irreversible phenomena.

In the second part of the paper, we have lifted the Irreversible Port Hamil-

tonian Systems to the Thermodynamic Phase Space which is canonically endowed with a contact structure associated with Gibbs' relation. For this class of systems we have suggested a lift which avoids any singularity of the contact Hamiltonian function and defines a control contact system on the complete Thermodynamic Phase Space, in contrast to the previously suggested lifts of such systems. Depending on the expression of the positive function γ in terms of the co-state variables, different lifts may be suggested which has been illustrated on the case of the CSTR dynamics.

In the third part, we firstly reminded different quasi-Hamiltonian formulations of the balance equations of a CSTR model, illustrating precisely the dependence of the structure matrices on the co-state variables. Secondly we have derived the formulation of the CSTR as an Irreversible Port Hamiltonian System and given the physical interpretation of the Poisson structure matrix in terms of the stoichiometry of the reaction, and have related the positive function γ with the irreversible entropy creation. Finally two alternative lifts of the CSTR model to a control contact system defined on the complete Thermodynamic Phase Space have been given.

Future work will aim at characterizing the dynamic properties of the Irreversible Port Hamiltonian Systems, in terms of stability and stabilization and the adaptation of the IDA-PBC stabilization methods (Ortega et al., 2002; Duindam et al., 2009) to this class of systems and their application to the control of the CSTR. Another interesting direction concerns the control of contact systems obtained by lifting the Irreversible Port Hamiltonian Systems to the complete Thermodynamic Phase Space. First results on the feedback control and stabilization of control contact systems (Ramirez et al., 2011a,c;

Ramirez, 2012) may be applied to this class of control contact systems. An important matter is the choice of the lift among all possible ones, which is adapted to ease the solutions of the PDE associated with the stabilization problem.

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